Chemical Durability of Glass-Ceramics

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Polycryatalline materials were prepared by heating glasses of the compositions, $Li_2O \cdot 1.5 SiO_2$, $Li_2O \cdot 2SiO_2$ and $Li_2O \cdot 3SiO_2$ and $Li_2O \cdot 3SiO_2 \cdot 0.1 M_mO_n$, where $M_mO_n = Na_2O$, K_2O, Al_2O_3 or ZrO_2, each with or without addition of platinum. They were exposed to various solutions, mainly to 5% HCl solution, at 90°±2°C for various periods.

The chemical durability of the polycrystalline materials, reported in terms of weight loss per unit of surface exposed, was correlated with their chemical composition, addition of platinum to their mother glasses and the kind of test reagent. Examination of the surface of the specimens before and after the durability test was also made by an X-ray diffractometer and an electron microscope in order to explain the result of the durability test in terms of the microstructure of the specimens.

INTRODUCTION

Polycrystalline materials produced from glasses are finding many applications as engineering materials and also as domestic wares. This is mainly due to their extraordinarily high mechanical strength and abrasion resistance. For their wider applications, however, their chemical durability is another important property, especially, for their use for chemical apparatuses.

The following reports of the studies on the latter property have appeared in recent years, but their number is still few. Moriya et al[1] reported the nature of chemical attack of diluted hydrofluoric acid on a crystallized glass of the $Li_2O \cdot 2SiO_2$ composition. Löcsei[2] studied the chemical durability of crystallized glasses in the system Na_2O-CaO-MgO-Al_2O_3-SiO_2 in relation to the effect of the amount of glassy phase.

In the present work, the results of chemical durabilty test on crystallized glasses of the Li_2O-SiO_2 system, mainly, to hydrochloric acids are described. Chemical durability is correlated with the chemical composition and microstructure of the body.

EXPERIMENTAL PROCEDURE

Glass Preparation

The glasses of the composition, $Li_2O \cdot 1.5SiO_2$, $Li_2O \cdot 2SiO_2$ and $Li_2O \cdot 3SiO_2$ and $Li_2O \cdot 3\ SiO_2 \cdot 0.1M_mO_n$, where $M_mO_n = Na_2O$, K_2O, Al_2O_3 or ZrO_2, each with varying

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concentrations of platinum, were prepared. The Pt was introduced into glass batches in the form of platinum chloride solution. The other raw materials used for the preparation of glass batches were lithium-, sodium- and potassium carbonate, aluminum hydroxide, zirconium oxide and potter's flint powders.

Batches to yield 100 gram glasses were prepared and melted in sintered alumina crucibles at 1300°~1400°C for two hours in an electric furnace with silicon carbide heating elements. Glass melts were poured on iron moulds, annealed, and cut in a form of rectangular plate of 30×30×2mm.

Crystallization

The glass specimens of the above size were ground with 1500-grit SiC powder to produce smooth surfaces, and then heated in the electric furnace on the schedule as shown in Fig. 1; the specimens were heated at a rate of 5°C/min. from room temperature to the final temperature except at the intermittions, i.e.,

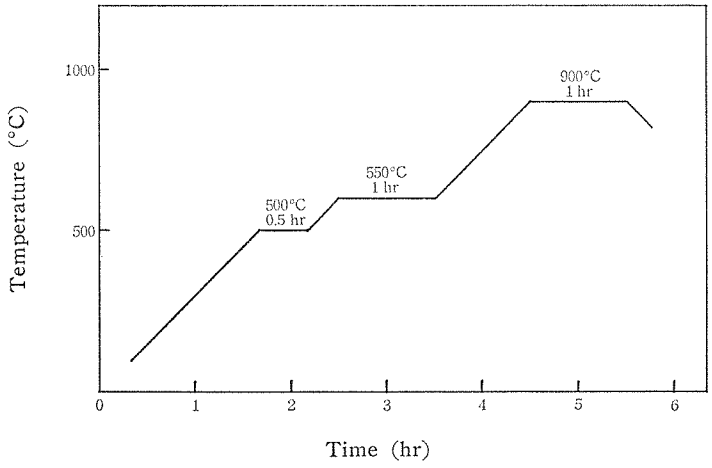


Fig. 1. Heating schedule for the crystallization of glasses.

at 500°C for 30min. and at 600°C for 1 hr.. The final temperature was 850°C for the glass specimens containing Na_2O and K_2O and 900°C for the others. At the final temperature the specimens were held for 1 hr. and then cooled at furnace rate.

Chemical Durability Test

Unless particularly mentioned, 5% HCl solution was used as the test reagent. Specimens of known weight and exposed surface (about 20cm²) were immersed in this solution at 90°±2°C for various periods. The specimens were then washed with distilled water, dried and reweighed. Durbility was represented in terms of weight loss per unit of surface exposed.

X-ray Diffraction and Electron Microscopy

Identification of polycrystalline phases separated out in the crystallized specimens was made by use of a Shimadzu X-ray diffractometer operated at 35KV

and 15mA. using nickel-filtered Cu K_α radiation. Diffraction patterns were run with the surfaces of plate specimens to be used for durability test.

Electron-microscopic observation of the surfaces of the specimens before and after durability test was made by the method of two-step replica of acetyl cellulose-carbon shadowed by chromium.

EXPERMENTAL RESULTS

Acid Resistance of Crystallized Specimens in the System Li_2O-SiO_2

Fig. 2 shows weight loss plotted versus time for the crystallized specimens in the system Li_2O-SiO_2 when treated with 5% HCl solution at 90°±2°C. Open circles represent data for the specimens crystallized without Pt and solid circles for the specimens containing 0.01 wt.% Pt as a nucleating agent. The figure indicates that the specimen containing Pt is always more resistant to acid solution than the specimen of the same basic composition but without Pt. For a series of specimens containing Pt, the durability decreases with the increase in the content of Li_2O, i.e., as the composition changes from $Li_2O \cdot 3SiO_2$ to $Li_2O \cdot 2SiO_2$ and further to $Li_2O \cdot 1.5SiO_2$. This relation, however, does not hold with the other series of specimens containing no Pt, i.e., the specimen of the composition $Li_2O \cdot 2SiO_2$ shows a greater weight loss than the other two specimens of the compositions $Li_2O \cdot 3SiO_2$ and $Li_2O \cdot 1.5\ SiO_2$.

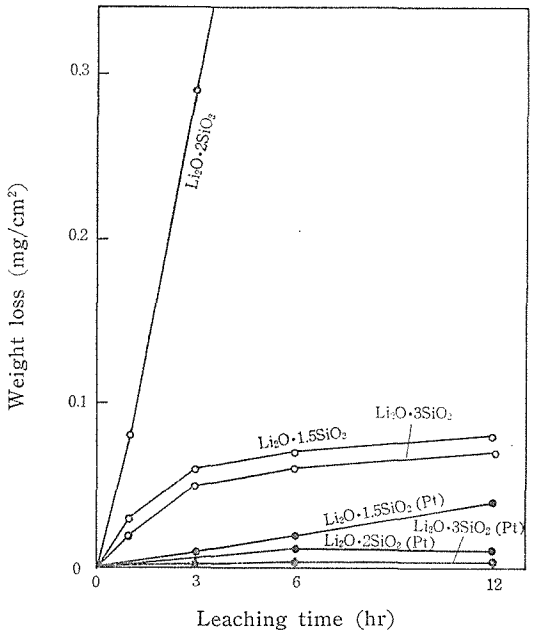


Fig. 2. Weight loss of the crystallized specimens in the system Li_2O-SiO_2 when treated with 5% HCl solution at 90°±2°C. The sign (Pt) refers to the specimens crystallized with platinum and no sign refers to the ones crystallized spontaneously.

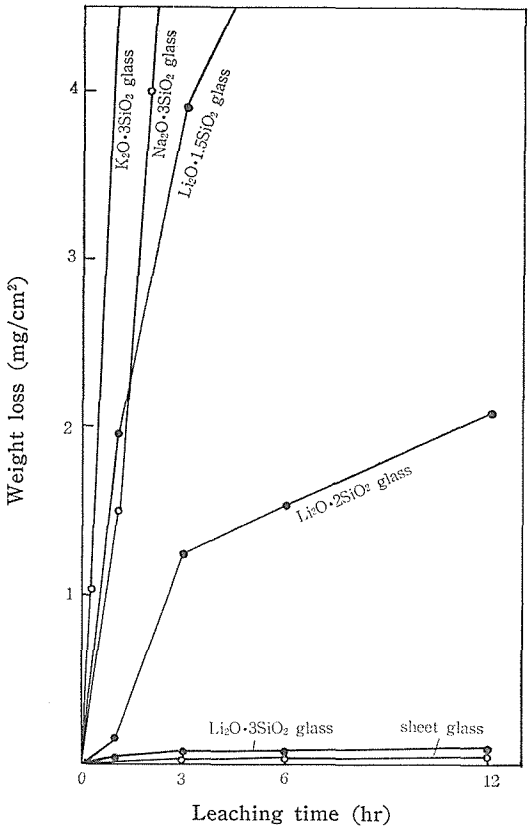


Fig. 3. Weight loss of the various glasses when treated with 5% HCl solution at 90±2°C.

Fig.3 shows the results of the durability tests made with the parent glasses of the crystallized specimens, the durability of which was already shown in Fig.2. Comparison of Fig.3 with Fig.2 indicates that for a series of specimens containing Pt, the crystallized specimens have always much higher chemical durability than the parent glasses of the same basic composition, respectively. This rule, however, does not hold for the specimens containing no Pt. In Fig.3 the results with glasses of the compositions $Na_2O \cdot 3SiO_2$ and $K_2O \cdot 3SiO_2$ and a sheet glass are also shown for reference.

Effect of Addition of Platinum on the Durability of $Li_2O \cdot 2SiO_2$ Crystallized Product

In Fig.4, the weight loss vs. time is shown for the specimens of the composition, $Li_2O \cdot 2SiO_2$, containing varying amounts of Pt. The durability increases with the increase in Pt concentration in the range from 0 to 0.005%.

Effect of Addition of the Third Component

The durability data for the crystallized specimens of the compositions $Li_2O \cdot 3SiO_2 \cdot 0.1M_mO_n$, where M_mO_n= Na_2O, K_2O, Al_2O_3 or ZrO_2, each containing 0.01% platinum, are shown in Fig.5. The data for the $Li_2O \cdot 3SiO_2$ specimen containing

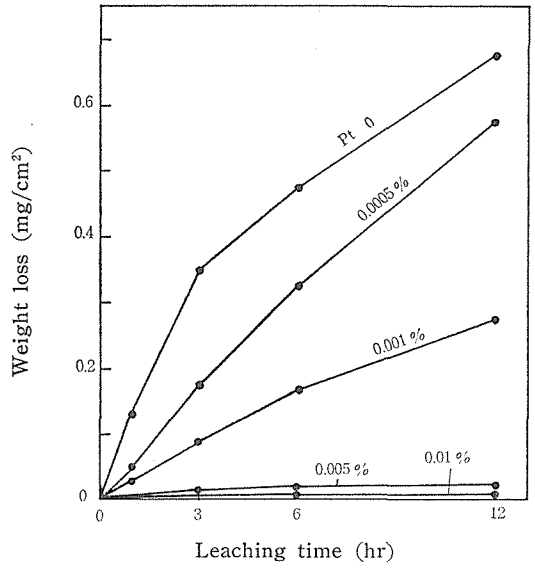


Fig. 4. Effect of the addition of platinum on the acid resistance of the crystallized specimen of the composition $Li_2O \cdot 2SiO_2$.

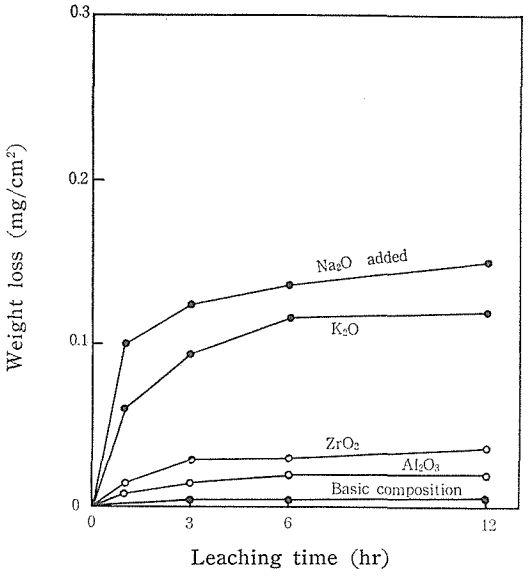


Fig. 5. Effect of additional components on the acid resistance of the crystallized specimen of the composition $Li_2O \cdot 3SiO_2$ with 0.01% Pt.

no third component is also shown for comparison. Of the third components introduced, the components Na_2O and K_2O brought a marked decrease in chemical resistance, i.e.,the weight loss, in 12 hr., for the $Li_2O \cdot 3SiO_2 \cdot 0.1Na_2O$ specimen is nearly 30 times as high as that for the $Li_2O \cdot 3SiO_2$ specimen.

Durability to Various Reagents beside HCl Solution

Durability to tap water and solutions of H_2SO_4, NaCl, Na_2CO_3 and NaOH, the concentration of which being all 5%, was also measured for the crystallized specimens of the composition $Li_2O \cdot 3SiO_2$ containing Pt. The results are shown in Fig. 6, in which the data of test using 5% HCl solution is reproduced. Generally, resistance to acidic and neutral solutions is much higher than to the alkaline solutions.

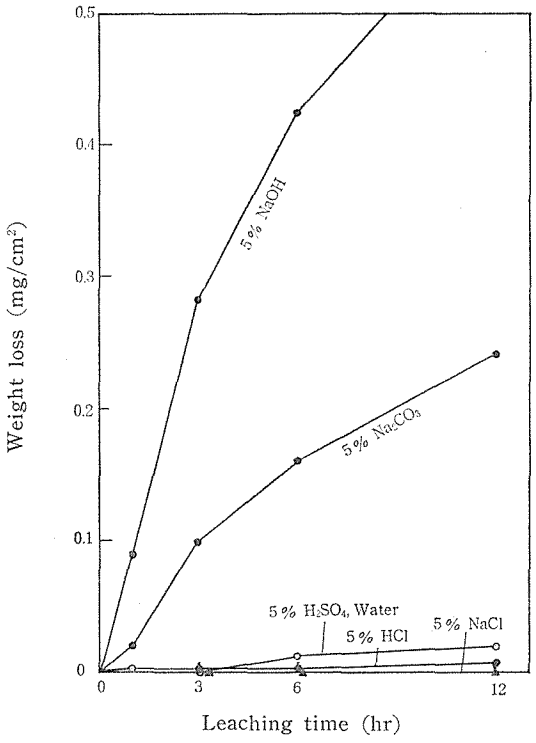


Fig. 6. Effect of various leaching solutions on the weight loss of the crystallized specimen of the composition $Li_2O \cdot 3SiO_2$ with 0.01% Pt.

X-ray Anaalysis and Visual Observation of the Surface of the Crystallized Specimens

(a) X-ray analysis. Crystalline phases in the specimens of various compositions identified by X-ray diffraction analysis are listed in Table 1. In all of the specimens investigated lithium disilicate was found to be the main crystalline phase. Beside this crystal, lithium metasilicate was found in the $Li_2O \cdot 1.5SiO_2$ specimen, and also various silica modifications such as quartz, cristobalite and tridymite were found in the $Li_2O \cdot 2SiO_2$ and $Li_2O \cdot 3SiO_2$ specimens.

The X-ray diffraction analysis gave no indication of the special effect of addition of Pt on the kind of crystal phase precipitated in the specimens, but gave a positive indication that the addition of Pt made a noticeable change in the direction of crystal growth. For the specimens containing Pt, the diffraction

Table 1. Crystalline phases found in crystallized specimens.

Composition	Crystalline phase*
$Li_2O \cdot 3SiO_2$	L2S, (Cr), (Q)
$Li_2O \cdot 3SiO_2$ (0.01% Pt)	〃
$Li_2O \cdot 2SiO_2$	L2S, (Cr)
$Li_2O \cdot 2SiO_2$ (0.01% Pt)	〃
$Li_2O \cdot 1.5SiO_2$	L2S, LS
$Li_2O \cdot 1.5SiO_2$ (0.01% Pt)	〃
$Li_2O \cdot 3SiO_2 \cdot 0.1Na_2O$ (0.01%Pt)	L2S, (Q)
$Li_2O \cdot 3SiO_2 \cdot 0.1K_2O$ (0.01% Pt)	L2S, (Tr). (Cr)
$Li_2O \cdot 3SiO_2 \cdot 0.1Al_2O_3$ (0.01% Pt)	L2S, (Q)
$Li_2O \cdot 3SiO_2 \cdot 0.1ZrO_2$ (0.01% Pt)	L2S, (Q)

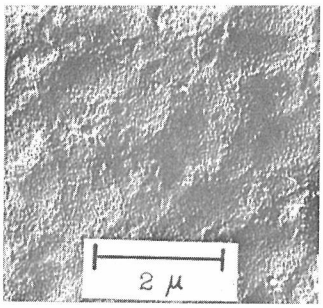
* L2S: Lithium disilicate, LS: Lithium metasilicte, Cr: Cristobalite, Q: Quartz, Tr: Tridymite. Parenthesis means a small amount of a given phase.

peaks observed were almost the same in intensity ratio as observed in the data reported[3] which was obtained with the same crystal specimen but in the form of powder. For the specimens containing no Pt, however, some deviations from the published data were observed with respect to their intensity ratio, i.e., the characteristic three peaks at d=3.60, 3.68 and 3.77, which had been reported, were not observed in the specimens of the present experiment and a peak at d=2.40 observed was unusually high. Hayami et al[4] and Rindone[5] reported that this difference can be explained to be due to crystal growing in the direction perpendicular to the surface of glass specimens, where cryatal nuclei are likely to form; if Pt is added to glass as a nucleating agent, nucleation would occur in the interior of glass as well as at the surface and so the orientation of precipitated crystals would be disturbed.

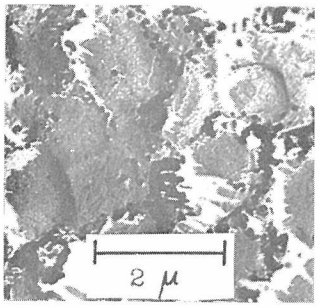
The diffraction pattern of the crystallized specimen containing Na_2O and K_2O were almost the same as that containing no these third components, but for the former small peaks at d=4.19, 4.00, 3.21 and 2.80 were observed, which would be some unknown non-silicate crystal phase separated out. It should be noted that these peaks, however, were not observed for the specimens, whose surface had been subjected to the durability test with HCl solution.

(**b**) **Electron microscopy.** The electron micrographs taken of the crystallized specimens of the two compositions $Li_2O \cdot 3SiO_2$ and $Li_2O \cdot 3SiO_2 \cdot 0.1Na_2O$, each containing 0.01wt% Pt, are shown in Fig.7. Adash mark refers to the surfaces after immersing in HCl solution for 5 hours and no mark those before the immersion.

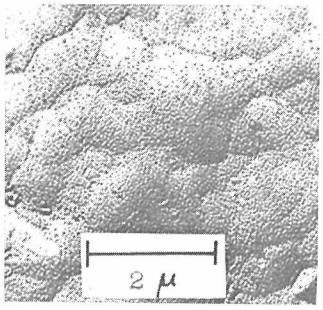
The big difference in appearance between a and b, which are respectively the photographs of the $Li_2O \cdot 3SiO_2$ and the $Li_2O \cdot 3SiO \cdot 0.1Na_2O$ specimen, both before the immersion in HCl solution, is the existence of black specks observed at the boundaries between large grains of silicate crystals in the sodium containing specimen b. Judging from their deep darkness, these black specks would be the shadows of some parts of the specimen, which had been stripped off from its surface, adhering to the replica film.



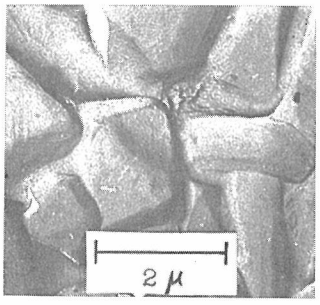
(a) Before treatment $Li_2O \cdot 3SiO_2$ (0.01% Pt added)



(b) Before treatment $Li_2O \cdot 3SiO_2 \cdot 0.1Na_2O$ (0.01% Pt added)



(a′) After treatment $Li_2O \cdot 3SiO_2$ (0.01% Pt added)



(b′) After treatment $Li_2O \cdot 3SiO_2 \cdot 0.1\ Na_2O$ (0.01% Pt added)

Fig. 7. Electron micrographs of the surface of crystallized specimens before and after the treatment with 5% HCl solution.

Comparison of the photographs of a′ and b′ with those of a and b indicates clearly that crystal boundaries become distinct by the acid treatment. This tendency is striking especially for the Na_2O containing specimen. The black specks observed in the photograph b cannot be found in that of b′.

(**c**) **Fuchsine test.** The crystallized specimens were immersed in a fuchsine dye solution at room temperature, and washed, dried, and examined for cracks. No cracks were observed on the surface for all of the specimens except for those of the $Li_2O \cdot 2SiO_2$ composition containing Pt in the amount less than 0.005wt%.

DISCUSSION

The experimental results described above can be explained if the mechanism of decomposition of the crystallized glasses of the Li_2O–SiO_2 system into HCl solution is assumed as follows: the lithium disilicate crystal, which is a main crystal phase separated out of the glasses of this system, has much higher chemical resistance to HCl solution than the glass of the same composition or even of the composition a little less in alkali content. Therefore, the chemical attack by HCl solution proceeds mainly along the grain boundaries between the lithium disilicate crystallites, and the rate of decomposition of the glassy phase, if it

remained at the grain boundaries, decides the chemical durability of the whole of the crystallized glass specimens. The alkali oxides such as Na_2O and K_2O, which were added to the $Li_2O \cdot 3SiO_2$ glass as the third component, are likely to remain in high concentration in the glassy phase at the grain boundaries, giving an extremely detrimental effect on the chemical resistance of this glassy phase; the black specks observed by the electron microscope at the crystal grain boundaries in the crystallized glass specimen containing Na_2O (Fig7b) would be the shadows of some sodium compounds, which were produced as a result of the reaction of the chemically reactive Na_2O rich glassy phase with carbon dioxide or water in atmosphere.

The occurrence of micro-cracks on the surface of the crystallized specimen, which were confirmed by fuchsine test especially for the specimens containing no or an extremely small amount of Pt, is an another factor which also deteriorates the chemical durability of the specimens. The micro-cracks have probably been formed by the big differences between the expansion coefficients of the two phases, the crystallites and the glassy matrix phase, or in crystallographic directions in the polycrystalline aggregate, and would increase the actual area of the specimen being in contact with HCl solution. The microstresses, which are likely to lead to the microcracks in the specimen, are known to be directly poportional to the grain size of the crystallites[6] and, therefore, the Pt, when added as a nucleating agent in the amount enough to decrease the size of the crystallites in the specimen, must improve its chemical dutability.

SUMMARY

Polycrystalline materials obtained from glasses of the compositions, $Li_2O \cdot 1.5SiO_2$, $Li_2O \cdot 2SiO_2$, $Li_2O \cdot 3SiO_2$, and $Li_2O \cdot 3SiO_2 \cdot 0.1\ M_mO_n$, where $M_mO_n = Na_2O$, K_2O, Al_2O_3 or ZrO_2, by mole ratio, each with or without platinum were exposed to various solutions, mainly to HCl solution, for various periods and their chemical durability was reported in terms of weight loss per unit of surface exposed. The effect of chemical composition of the crystallized materials, addition of platinum to their mother glasses and the kind of test reagent on their chemical durability may be summarized as follows.

(1) For the crystallized specimens of the two component system, i.e., $Li_2O \cdot 1.5SiO_2$, $Li_2O \cdot 2SiO_2$, and $Li_2O \cdot 3SiO_2$, the durability, in general, increased with the increase in SiO_2 content, regardless of the presence of Pt. The durability of the crystallized spceimens was much higher than that of their mother glasses. An exception was the $Li_2O \cdot 2SiO_2$ crystallized specimen without Pt, which showed the very low durability.

(2) The poor durability of the $Li_2O \cdot 2SiO_2$ specimen was concluded to be due to the presence of micro-cracks on the surface of the crystallized specimen. The addition of Pt as a nucleating agent in a appropriate amount (0.005~0.01% by weight) was found effective in suppressing the development of the micro-cracks during reheating, and thus improving the durability.

(3) Of the four components, Na_2O, K_2O, Al_2O_3 and ZrO_2, alkali oxides lowered the durability of the specimens markedly. This was attributed to concentration

of these components in grain-boundary regions in the crystallized specimens.

(4) The durability tests made with the crystallized glass of the composition $Li_2O \cdot 3SiO_2$ containing 0.01% Pt using various test reagents such as tap water, 5% HCl, 5% H_2SO_4, 5% NaCl, 5% NaOH and 5% Na_2CO_3 showed that, in general, the attack of alkaline solutions was much severe than that of the neutral and acidic solutions.

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